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We have prepared several poly(orthoformate) polymers, which endothermically decompose in the presence of acid.

We have prepared ABA block copolymers using poly(orthoformates) and BAMO as the blocks and studied their LOVA properties.

We have devised a simple, economical approach to the synthesis of polynitramine binders over those taken previously. We obtain complete control of the molecular weight by first preparing a well characterized polymer which is then nitrolyzed to give a polynitramine. In this program, we have investigated different combinations of block copolymers and side-chain substitutions on the polymer to overcome the crystallinity problems of polynitramines and to give a binder with the necessary mechanical properties.

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SYNTHESIS OF ENERGETIC ACID LABILE LOVA BINDERS

Subhash C. Narang
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SRI Project 2092

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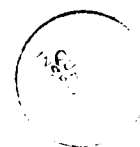Washington, DC 20332-6448

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CONTENTS

SUMMARY

The objective of this research is to prepare binders for use in low vulnerability (LOVA) applications. During this project, we have been exploring the synthesis of several LOVA polymers based on totally aliphatic polycarbonates, ABA block copolymers, and polyethyleneimine block copolymers as thermoplastic elastomers. These polymers have possible application as binders in explosive or propellant formulations. We have also been synthesizing polyorthoester block copolymers, which endothermically decompose in the presence of acids, as alternative LOVA binders. We have prepared ABA block copolymers with a poly(bis-(azidomethyl)oxetane) (BAMO) B-block and polycyclohexane dimethanol orthoformates as the A block and a completely polycarbonate ABA block copolymer. In summary, our work over the last three years has focused on the following:

- We have prepared several totally aliphatic polycarbonate blocks and measured their glass transition temperatures and melting points. We have performed differential scanning calorimetry (DSC) to test the ability of these polymers to endothermically decompose in the presence of acid and/or heat. We have linked these blocks to give us an aliphatic polycarbonate ABA block copolymer.

- We have prepared several poly(orthoformate) polymers, which endothermically decompose in the presence of acid.

- We have prepared ABA block copolymers using poly(orthoformates) and BAMO as the blocks and studied their LOVA properties.

We have devised a simple, economical approach to the synthesis of polynitramine binders over those taken previously. We obtain complete control of the molecular weight by first preparing a well characterized polymer which is then nitrolyzed to give a polynitramine. In this program, we have investigated different combinations of block copolymers and side-chain substitutions on the polymer to overcome the crystallinity problems of polynitramines and to give a binder with the necessary mechanical properties.

Polymer binders affect all aspects of performance and properties of propellants and explosives. Although, a significant amount of research has been devoted to GAP, polyacrylates, and polyoxetanes, new polymeric binders are required with superior mechanical properties due to the very high solids loading requirements of current propellant and explosive formulations (up to 80% w/w), chemical stability to oxidizer ingredients such as ammonium perchlorate, HMX, or

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RDX. Furthermore, in addition to good mechanical properties, the polymeric binder should contain energetic functional groups to increase the energy density and hence improve the detonation velocity (D_{vel}) and the detonation pressure (P_{cj}) in explosive formulations or the specific impulse (I_{sp}) in propellant applications. Finally, a lowering of the vulnerability of the final formulation is required to decrease the sensitivity of materials to premature detonation due to shock or thermal stress. The nitramine group is one of the most stable energetic groups, it is thermally, shock, and hydrolytically stable, certainly more stable than nitrate esters or azides. A polynitramine polymer will be chemically compatible with current energetic materials such as HMX or RDX.

The goal of the proposed program is to develop synthesis routes to new binder materials which are thermoplastic elastomers (TPEs) to give good mechanical properties and which contain an energetic group to improve the performance. It is also important that these materials be easily prepared in only a few steps from inexpensive materials which have a commercial basis with as low a sensitivity in the final formulation as possible, if possible including low vulnerability (LOVA) characteristics. Successful completion of these studies will greatly enhance binder effectiveness and ultimately impact a broad range of propellants and explosives.

RESULTS AND DISCUSSION

SYNTHESIS OF HARD AND SOFT BLOCK POLYCARBONATES

The soft block segments were synthesized from linear aliphatic diols such as propane-1,3,-diol and decane-1,10-diol via reaction with phosgene in the presence of an acid acceptor. The resulting oligomers displayed the desired low glass transition temperatures ranging from -88°C to -42°C as listed in Table 1. These oligomers later served as models for the energetic soft segment blocks. All the soft blocks have glass transition temperatures well below the currently accepted requirements.
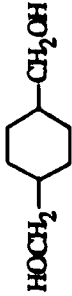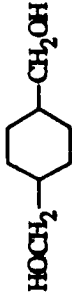
The hard block polycarbonates were synthesized from cis-, transcyclohexane-1,4-dimethanol and 2,2,4,4-tetramethylcyclobutane-1,3-diol by reaction with phosgene and an acid acceptor. The melting points are 85°-90°C and 206°C, respectively (Table 1). The resulting block copolymers will thus provide a desirable combination of low glass transition temperature and easy melt processability. LOVA characteristic are imparted to the aliphatic polycarbonates by virtue of the ease of endothermic depolymerization at ~ 130°-150°C.

Because of the high melting point of the tetramethylcyclobutanediol polycarbonate, we decided to concentrate initially on the cyclohexanedimethanol derived polycarbonate as the hard block. The molecular weight of the blocks was controlled by using nonstoichiometric amounts of the diol and phosgene. When phosgene was used in excess, the polycarbonate blocks were obtained easily with a functionality of two. When the diol was used in excess, it was more difficult to purify the block from excess diol reactant. During the isolation process, however, the chloroformate-terminated blocks sometimes decomposed to yield halide terminated end groups, instead of the desired hydroxyl terminal group. This problem was particularly pronounced for the cyclobutanediol derivate.
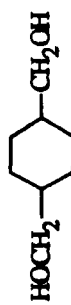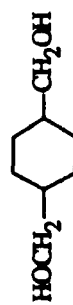
SYNTHESIS OF POLY(ORTHOFORMATES)

The poly(orthoformates) are prepared by the method of Heller et al. Poly(orthoformates) prepared by this method are known to depolymerize in the presence of acids. The synthesis of the poly(orthoformates) involves the reaction of a diol with 3,9-bis(ethylidene2,4,8,10-tetraoxaspiro[5,5]undecane) [DETASU].

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Table 1: Thermal Decomposition of Poly(carbonates) and Poly(orthoformates)

Starting Diol	Acid Added	Decomposition Onset (°C)[a]	Percent Acid	Endothermic Decomposition[b]	M_N	M_W
Poly(carbonate) Blocks						
HOCH$_2$–cyclohexyl–CH$_2$OH	None	320	0	Yes	1913	2077
HOCH$_2$–cyclohexyl–CH$_2$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	172	1	Yes	1913	2077
HOCH$_2$–cyclohexyl–CH$_2$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	85	10	Yes	1913	2077
HO(CH$_2$)$_6$OH	None	315	0	Yes	4559	6168
HO(CH$_2$)$_6$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	135	1	Yes	4559	6168
HO(CH$_2$)$_6$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	85	10	Yes	4559	6168
HO(CH$_2$)$_8$OH	None	333	0	Yes	8191	18006
HO(CH$_2$)$_8$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	305	1	Yes	8191	18006
HO(CH$_2$)$_8$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	215	10	Yes	8191	18006
HO(CH$_2$)$_{10}$OH	None	320	0	Yes	6883	4664
HO(CH$_2$)$_{10}$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	225	1	Yes	6883	4664
HO(CH$_2$)$_{10}$OH	p-CH$_3$C$_6$H$_4$SO$_3$H	181	10	Yes	6883	4664
HOCH$_2$CH=CHCH$_2$OH	None	152	0	Yes	c	

Structure	Catalyst					
HO–[CH$_2$C≡CCH$_2$OCO]$_n$ (O)	None	237	0	No	-	-
HO–[CH$_2$C≡CCH$_2$OCO]$_n$ (O)	p-CH$_3$C$_6$H$_4$SO$_3$H	165	10	No	-	-
CH$_3$ CH$_3$ O / HO–[CHC≡CCHOCO]$_n$	None	228	0	No	1094	2224
CH$_3$ CH$_3$ O / HO–[CHC≡CCHOCO]$_n$	p-CH$_3$C$_6$H$_4$SO$_3$H	141	10	No	1094	2224
NO$_2$ O / [CH$_2$CCH$_2$OCO]$_n$ CH$_3$	None	198	0	Yes	-	-
HO–[CH$_2$–⟨C$_6$H$_4$⟩–CH$_2$OCO]$_n$ (O)	None	179	0	Yes	-	-

Polyorthoformate Block

Structure	Catalyst			
HOCH$_2$–⟨cyclohexane⟩–CH$_2$OH	None	343	0	Yes
HOCH$_2$–⟨cyclohexane⟩–CH$_2$OH	CH$_3$CO$_2$H	Room Temp.	1	Yes
HOCH(CH$_3$)CH$_2$CH$_2$CH$_2$CH(CH$_3$)OH	None	240	0	Yes

a TGA, 5% weight loss
b DSC
c Soluble in CHCl$_3$, insoluble in THF

Using this method, we have synthesized a number of poly(orthoformates). We have prepared poly(orthoformate) blocks from the diols cyclohexane dimethanol, 2,5-hexanediol, and 1,10-decanediol as well as an ABA block copolymer made from a poly(bis(azidomethyl)oxetane) center block with poly(decaneorthoformate) and a ABA block copolymer from the A-block poly(cyclohexanedimethanolorthoformate) and the B-block poly(decaneorthoformate).

THERMAL DECOMPOSITION OF POLYMER BLOCKS

Table 2 shows the thermal degradation properties of the poly(carbonates) and the poly(orthoformates) in the presence and absence of acid. Both types of polymers show strong endothermic peaks, signifying their thermal decomposition upon the addition of acids. This is exactly the type of behavior desired from a LOVA polymer. The only exception to this strong endothermic decomposition was the thermal decomposition of the cyclohexane dimethanol polycarbonate in the presence of p-toluene sulfonic acid. Further studies are under way to elucidate this anomalous result.

These studies were done by adding a small amount of acetic acid, chloroacetic acid, or p-toluene sulfonic acid to the polymer in the presence of a solvent to ensure good mixing of the acid in the polymer. The solvent was then stripped off, and the samples were monitored by differential scanning calorimetry (DSC).

SYNTHESIS OF A-B-A POLYCARBONATE COPOLYMERS

The polycarbonate blocks had sufficient impurities of diol and moisture, that the bisisocyanate method for synthesizing the A-B-A blocks copolymers from isolated blocks, was not successful in our hands, despite trying a large variety of experimental conditions. In order to alleviate these problems associated with chlorodecarboxylation and moisture contamination, it was decided to use the simpler one pot approach.

As an example, the soft block was synthesized via reaction of 1,10-decanediol with 10% excess phosgene followed by the addition of cyclohexanedimethanol and phosgene to achieve the synthesis of the desired block copolymers.

The reaction was monitored carefully using gel permeation chromatography. The block copolymer was purified thoroughly by repeated precipitation and analyzed further by GPC, NMR, IR and thermal analysis techniques.

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Table 2: Thermal Decomposition of ABA Block Copolymers

Polymer	Acid Added	Decomposition Onset (°C)[a]	Percent Acid	Endothermic Decomposition[b]	M_N	M_W
$[CH_2\!-\!\langle\rangle\!-\!CH_2OCO]_n\text{-}[(CH_2)_{10}OCO]_m\text{-}[CH_2\!-\!\langle\rangle\!-\!CH_2OCO]_n$	None	235	0	Yes	5402[c,d]	10212
$[CH_2\!-\!\langle\rangle\!-\!CH_2OCO]_n\text{-}[(CH_2)_{10}OCO]_m\text{-}[CH_2\!-\!\langle\rangle\!-\!CH_2OCO]_n$	p-CH₃C₆H₄SO₃H	185	1	Yes	5402	10212
$[CH_2\!-\!\langle\rangle\!-\!CH_2OCO]_n\text{-}[(CH_2)_{10}OCO]_m\text{-}[CH_2\!-\!\langle\rangle\!-\!CH_2OCO]_n$	p-CH₃C₆H₄SO₃H	160	10	Yes	5402	10212

a TGA, 5% weight loss
b DSC
c Poly[cyclohexane-1,4-dimethanol carbonate] M_N = 2600
d Poly[decanecarbonate] M_N = 4670
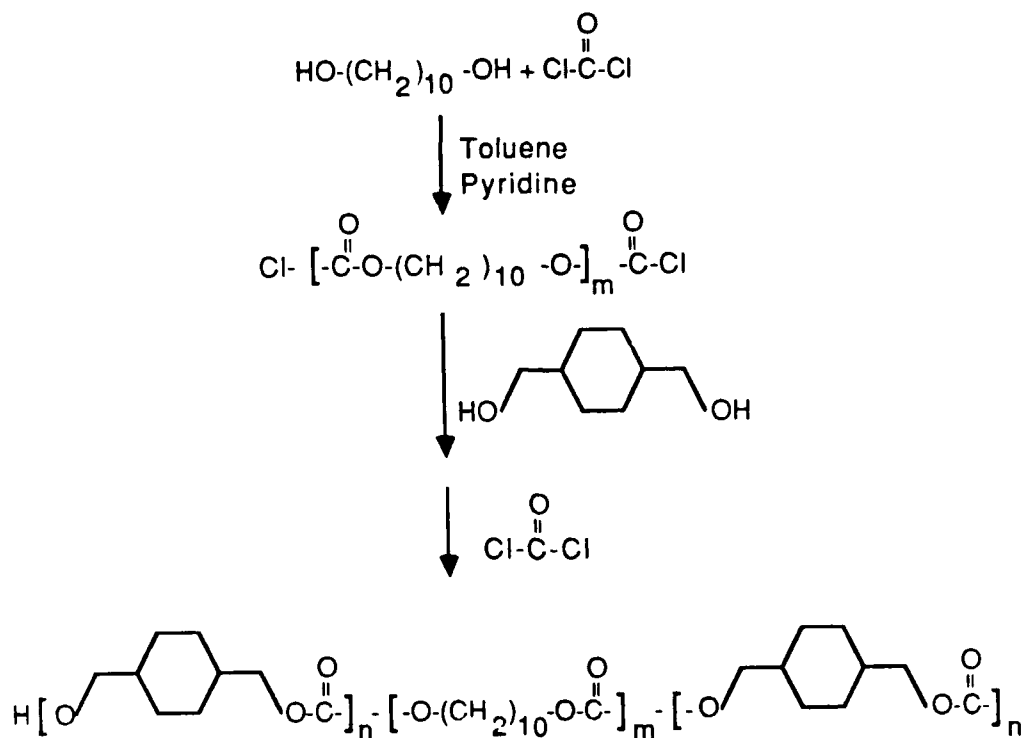
SYNTHESIS OF POLY(ORTHOFORMATE)-POLY(BAMO) AND POLYCARBONATE-POLYBAMO ABA BLOCK COPOLYMERS

We have prepared ABA block copolymers from cyclohexane dimethanol poly(orthoformate) as the A block and poly(BAMO) as the B-block (BAMO is bis(azidomethyl)oxetane).

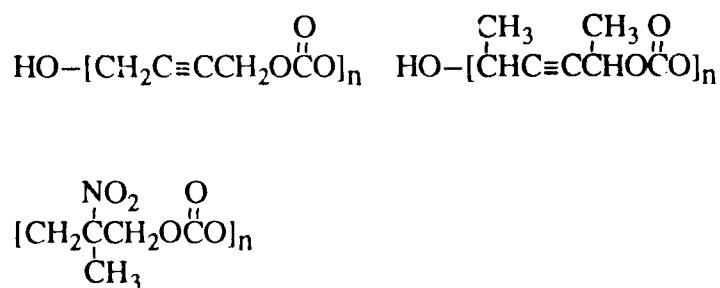A DSC of these ABA polymers gave a exothermic decomposition upon heating. Following this result, we ran DSCs of several other BAMO/polycarbonate or BAMO/polyorthoformate mixtures In all cases, we observed that the DSC is identical to the DSC of BAMO alone We concluded that the polyorthoformates and polycarbonates that we have prepared have too high a decomposition temperature to halt the exothermic decomposition of BAMO

Therefore, we decided to prepare polycarbonates that have decomposition temperatures near 200°C so that the polycarbonate polymer is the first to decompose The next set of polycarbonates was synthesized from secondary tertiary and allylic diols instead of primary diols to give the lower decomposition temperatures

POLYCARBONATE BLOCKS WITH LOWER DECOMPOSITION TEMPERATURE

We decided to focus on the preparation of polycarbonate hard blocks which have a lower decomposition temperature in the presence of acid than previously observed and which contain energetic groups or at least groups with a positive heat of formation in the polymer backbone. Acetylenic groups have a high, positive heat of formation and we believed that they would make good polycarbonate A-blocks. Consequently, we have synthesized polycarbonate blocks from two acetyenic diols, 2-butyne-1,4-diol and 1,4-dimethyl-2-butyne-1,4-diol as well as the nitro containing 2-methyl-2-nitropropane-1,3-diol.

$$HO-[CH_2C \equiv CCH_2O\overset{\overset{\displaystyle O}{\|}}{C}O]_n \qquad HO-[\overset{\overset{\displaystyle CH_3}{|}}{C}HC \equiv C\overset{\overset{\displaystyle CH_3}{|}}{C}HO\overset{\overset{\displaystyle O}{\|}}{C}O]_n$$

$$[CH_2\overset{\overset{\displaystyle NO_2}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2O\overset{\overset{\displaystyle O}{\|}}{C}O]_n$$

Poly[2-butyne-1,4-diol-carbonate] was insoluble in THF so it was not possible to determine the molecular weight. Consequently, we synthesized poly[1,4-dimethyl-2-butyne-1,4-diol-carbonate] which has much better solubility while still having hard block character (high melting point). Poly[2-butyne-1,4-diol-carbonate] and poly[1,4-dimethyl-2-butyne-1,4-diol-carbonate] have a thermal decomposition temperature greater than 230°C and show a exothermic

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decomposition. A much lower decomposition temperature is noted when p-toluene sulfonic acid is added, reducing the decomposition temperature to 165 and 138°C respectively. This compares favorably to poly[cyclohexane-1,4-dimethanol-polycarbonate] which has a thermal decomposition of 320°C in the absence of acid, but lowering to 172 and 85°C with the addition of 1 and 10 wt.% p-toluene sulfonic acid respectively. Table 1 has a complete list of all the polycarbonate blocks we have synthesized thus far.

Our polycarbonate containing an energetic group, poly[2-methyl-2-nitropropane-1,3-diol-carbonate], was synthesized. This polycarbonate has a onset for thermal decomposition at 198°C with a sharp endothermic decompositon as shown by DSC.

Finally, we have synthesized a polycarbonate based on 1,4-benzenedimethanol. This polycarbonate was made as a model system for the ultimate synthesis of nitroaromatic containing polycarbonates such as poly[2-nitro-1,4-benezenedimethanol-carbonate] or poly[2,5-dinitro-1,4-benezenedimethanol-carbonate] shown below.

$$HO-[CH_2-\langle C_6H_4 \rangle-CH_2OC(=O)O]_n$$

$$HO-[CH_2-\langle C_6H_3(NO_2) \rangle-CH_2OC(=O)O]_n$$

$$HO-[CH_2-\langle C_6H_2(NO_2)(O_2N) \rangle-CH_2OC(=O)O]_n$$
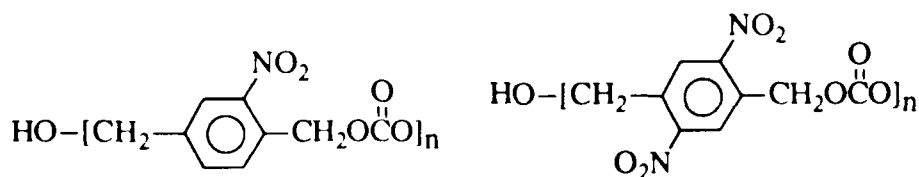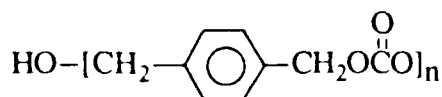
These nitroaromatic polycarbonates should make excellent hard blocks containing energetic groups. Poly[1,4-benzenedimethanol-carbonate] has a reasonably low thermal decomposition temperature of 179°C in the absence of acid.

ENERGETIC MATERIAL PROPERTIES OF POLYCARBONATES

We have done KJSM calculations to determine the effect of adding energetic groups to the polycarbonate system. We show below the results of these calculations for the nitro substituted polycarbonate system that we have prepared, poly[tetranitrohexane carbonate]. Also included in this table is the proposed polymeric binder material poly[bis[nitromethyl]oxetane] (BNMO) and

two oxidizers trinitrotoluene (TNT) and trinitrobenzene (TNB)

Table1

CALCULATED PROPERTIES OF POLYCARBONATES VERSUS OTHER ENERGETIC MATERIALS

Compound	Detonation Pressure (Kbar)	Detonation Velocity (mm/μs)	Density (g/cm^3)
Poly[tetranitro-hexanediol carbonate]	7.3	219	1.7
Poly(bisnitromethyl-oxetane)	5.7	73	1.5
Trinitrobenzene	7.3	223	1.7
Trinitrotoluene	6.7	166	1.6

Heat of formation of tetranitrohexanediolpolycarbonate is calculated to be -181.14

As you can see from this table, the proposed energetic polycarbonate, poly[tetranitrohexanediolcarbonate], does quite well when compared to other energetic materials. As a consequence, the use of a polycarbonate binder system is not an energy drain on the overall system. Indeed, such polycarbonates can instead be an asset for improving performance of the system.

POLY[ETHYLENEIMINE] BASED MATERIALS (POLYNITRAMINES)

We have been working on a parallel effort to synthesize binders containing the insensitive nitramine functionality. Initially, we have prepared a polynitramine (1), ([N(NO$_2$)CH$_2$CH$_2$]$_n$) or poly(ethylenenitramine), in high yield in one step.

$$\underset{\substack{\displaystyle| \\ \text{C}=\text{O} \\ \displaystyle| \\ \text{C}_2\text{H}_5}}{(\text{NCH}_2\text{CH}_2)_n} \xrig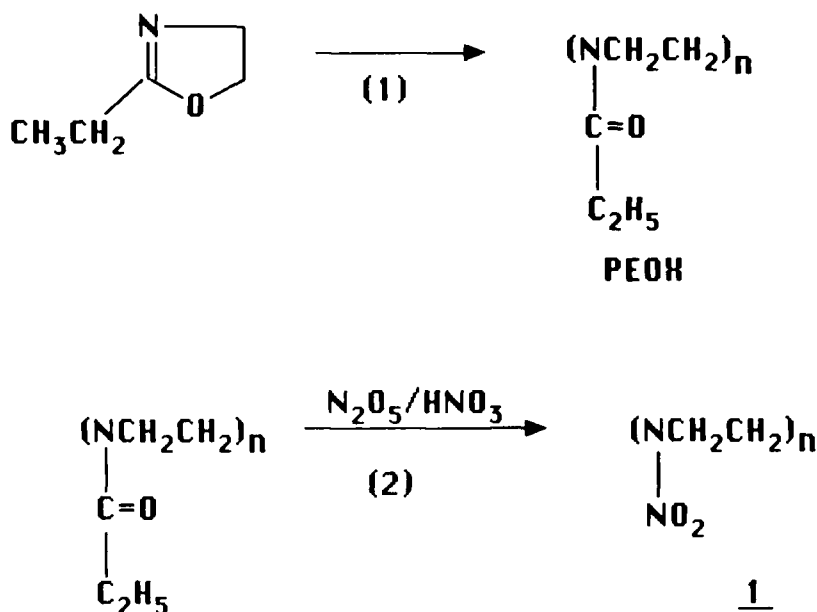htarrow{\text{N}_2\text{O}_5/\text{HNO}_3} \underset{\substack{\displaystyle| \\ \text{NO}_2}}{(\text{NCH}_2\text{CH}_2)_n}$$
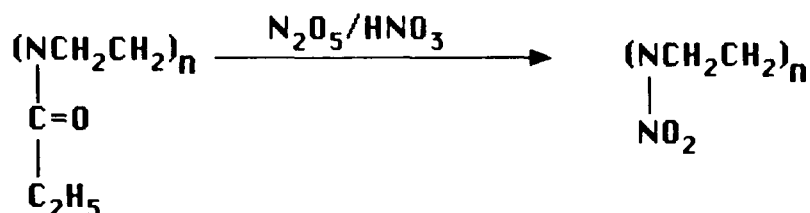
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Compound 1 is a promising candidate as an energetic block for an ABA copolymer because of the high percentage of nitramine groups incorporated into the polymer. Several attempts have been made previously[6,7] to prepare polynitramines but without much success; the major difficulties were (1) the inability to reproduce the molecular weight and (2) the high crystallinity of the polynitramine.

Compared with previous approaches, our approach is a simple, economical method for synthesizing polynitramine binders. Poly[ethyloxazoline] is a well-known thermoplastic elastomer that is sold under the trade name PEOX[TM]. PEOX[TM] is commercially available from Dow Chemical ($3.15/lb). PEOX[TM] is easily prepared with a known molecular weight and is currently sold in three molecular weight ranges: 50,000, 200,000, and 500,000. In addition, polymers of lower molecular weight can be prepared easily by ring opening polymerization of 2-methyl and 2-ethyloxazolines. Hence, by nitrolysis of a polymer of known molecular weight, we can obtain a polynitramine with known molecular weight.

$$\text{CH}_3\text{CH}_2 - \underset{O}{\overset{N}{\diagup}} \xrightarrow{\quad (1) \quad} \begin{array}{c} (\text{NCH}_2\text{CH}_2)_n \\ | \\ \text{C}=\text{O} \\ | \\ \text{C}_2\text{H}_5 \end{array}$$

<div align="center">PEOH</div>

$$\begin{array}{c} (\text{NCH}_2\text{CH}_2)_n \\ | \\ \text{C}=\text{O} \\ | \\ \text{C}_2\text{H}_5 \end{array} \xrightarrow[\quad (2) \quad]{\text{N}_2\text{O}_5/\text{HNO}_3} \begin{array}{c} (\text{NCH}_2\text{CH}_2)_n \\ | \\ \text{NO}_2 \end{array}$$

<div align="center">**1**</div>

THEORETICAL PERFORMANCE OF ENERGETIC POLYMERS

Table 1 compares the calculated performance characteristics of Compound **1** versus other binders and oxidizers currently considered for use. These values were calculated using the Kamlet-Jacobs-Simplified-Method (KJSM). In this calculation, detonation velocity (D_{vel}) is consistently underestimated, and the detonation pressure, P_{cj}, is slightly overestimated when compared to measured values, which we have included for comparison. The D_{vel} and P_{cj} values of Compound **1** are considerably better than those for either BAMO/BNMO or BAMO/AMMO, which are being considered as possible energetic binders (Table 1). The calculated energy output is not as high as that of HMX or RDX, but would not be expected to be; surprisingly, Compound **1** is more energetic than TNT. Thus, if used as a binder material, Compound **1** would not be a drain on the overall energy output of any system.

TABLE 2

CALCULATED PROPERTIES OF BINDERS AND OXIDIZERS

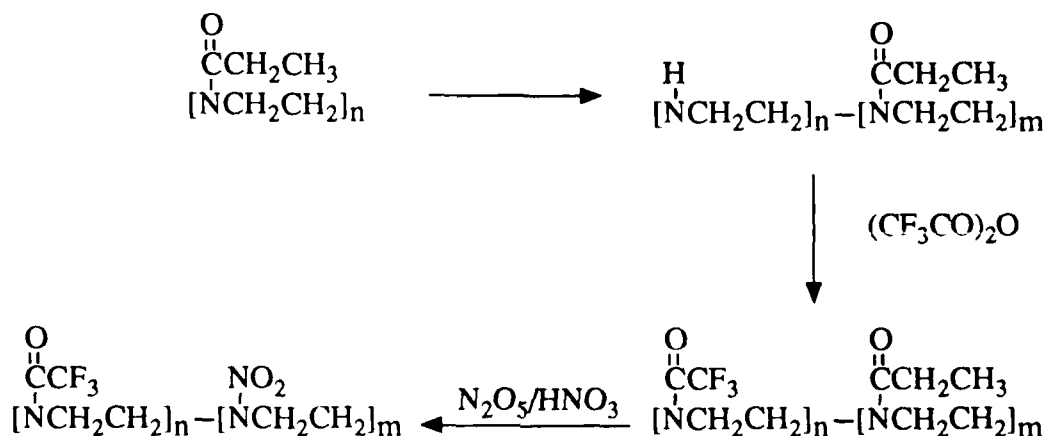| Compound	D_{vel} (mm/μs)	P_{cj} (kbar)	ΔH_{rxn} (kcal/mole)	$\Delta H_{f, Prod}$ (kcal/mole)	$\Delta H_{f, SM}$ (kcal/mole)	Density (g/cc)
Calculated Values						
Compound 1	7.0	201.0	-120.1	-115.6	4.5	1.6
BAMO/AMMO	4.9	85.3	-937.9	-578.0	359.9	1.3[a]
BAMO/BNMO	6.4	167.0	-235.7	-231.2	4.5	1.5[a]
HMX	9.3	392.0	-354.7	-336.8	17.9	1.9
RDX	8.0	341.0	-267.3	-252.6	14.7	1.8
TNT	7.6	241.6	-228.3	-236.9	-8.6	1.6
Measured Values for Known Oxidizers						
HMX	9.11	387	-	-	-	1.9
RDX	7.25	338	-	-	-	1.77
TNT	6.93	190	-	-	-	1.64

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[a]Density from Russ Reed, NWC China Lake.

However, despite the good energetic properties of Compound 1, we have found that it does not have the necessary mechanical properties to make it an excellent binder by itself. Compound 1 melts with decomposition at ~260°C. Because of the high melting point, it would be difficult to process any formulation containing compound 1. Therefore, we are currently concentrating on variants of compound 1, containing substituted monomers that disturb the symmetry of the backbone and thus lower the melting point.

Such a polymeric nitramino compound has many attractions. It is an easy way to introduce energetic groups and would be highly stable. Unfortunately, the product has the same physical properties as brick dust.

We have developed routes to other derivatives which include the presence of a nitramine

group in the molecule. One of the more promising routes is to prepare a copolymer of nitramino groups with some other, more tractable grouping. For this synthesis, our initial work has focused on the synthesis of a random copolymer of nitramino groups and N-trifluoroacetyl groups. We believe that the trifluoroacetyl group will act to soften the resulting polymeric product thus giving us a material with reasonable material properties for application as a binder.

We have synthesized the first of these polymers by the route shown below starting with a PEOX polymer of nominal 50,000 molecular weight.

$$
\begin{array}{ccc}
\overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{C}}CH_2CH_3} & & H \quad \overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{C}}CH_2CH_3} \\
[\overset{|}{N}CH_2CH_2]_n & \longrightarrow & [\overset{|}{N}CH_2CH_2]_n-[\overset{|}{N}CH_2CH_2]_m
\end{array}
$$

$(CF_3CO)_2O$

$$
\begin{array}{ccc}
\overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{C}}CF_3} \quad \overset{\displaystyle NO_2}{\underset{\displaystyle |}{}} & & \overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{C}}CF_3} \quad \overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{C}}CH_2CH_3} \\
[\overset{|}{N}CH_2CH_2]_n-[\overset{|}{N}CH_2CH_2]_m & \xleftarrow{\quad N_2O_5/HNO_3 \quad} & [\overset{|}{N}CH_2CH_2]_n-[\overset{|}{N}CH_2CH_2]_m
\end{array}
$$

We have recently obtained the first results from this strategy. A random copolymer containing N-nitro and N-trifluoroacetyl groups has been synthesized. However, thermal properties have not yet been measured nor has the molecular weight of the product been determined.
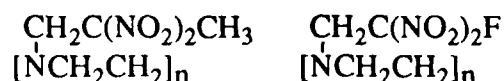
Studies are underway to efficiently control the degree of hydrolysis of the propionyl groups from the backbone of PEOX. We have examined the possibility whether we can nitrate first, replacing only a known fraction of the propionyl groups. We have been successful in controlled partial nitrolysis of PEOX with N_2O_5/HNO_3 to yield random copolymers of ethyloxazoline and N-nitroethyleneimine. Various ratios of n and m have been synthesized (n/m = 5/1 to 1/5). As the concentration of nitro groups increases, the solubility of the polymer in common organic solvents decreases. Above 80% nitration, the polymer is insoluble in most solvents.

The advantages of this method are that it utilizes inexpensive, commercially available starting polymers that can be converted in one step into energetic binders. It is a highly versatile

process because the extent of reaction can be controlled easily. These polymers are easily processable with a significant energy content.

Several other highly energetic derivatives of poly[ethyleneimine] have been prepared. Unfortunately, the stability of these compounds is poor and they cannot be considered as potential binders. They are nevertheless good examples of simple transformations of an inexpensive starting material to give energetic materials.

Starting with poly[ethyleneimine], we have prepared poly [N-(ß,ß-dinitro-ß-fluoroethyl)ethyleneimine], and poly [N-(ß,ß-dinitropropyl)ethyleneimine] as shown below.

$$CH_2C(NO_2)_2CH_3 \quad CH_2C(NO_2)_2F$$
$$[NCH_2CH_2]_n \quad\quad [NCH_2CH_2]_n$$

We had hoped that these materials would be useful as efficient binders that are internally plasticized for use in propellant or explosive formulations. Unfortunately, the thermal decomposition temperature of these compounds is too low. The results of the DSC studies are shown below.
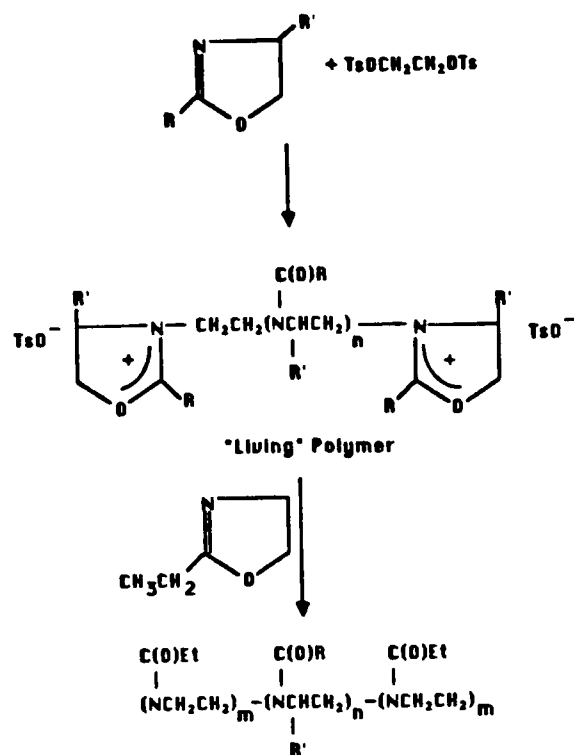
Compound	Decompostion Temperature °C (DSC)
NO_2 $[NCH_2CH_2]_n$	270
$CH_2C(NO_2)_3$ $[NCH_2CH_2]_n$	
$CH_2C(NO_2)_2CH_3$ $[NCH_2CH_2]_n$	110
$CH_2C(NO_2)_2F$ $[NCH_2CH_2]_n$	105

These compounds decompose by a reverse of the Mannich reaction which is used for their synthesis. The backbone nitrogen apparently has too much electron density which destabilizes the polymer. We are considering what modifications could be made to the polymer backbone to obtain usable binder materials.
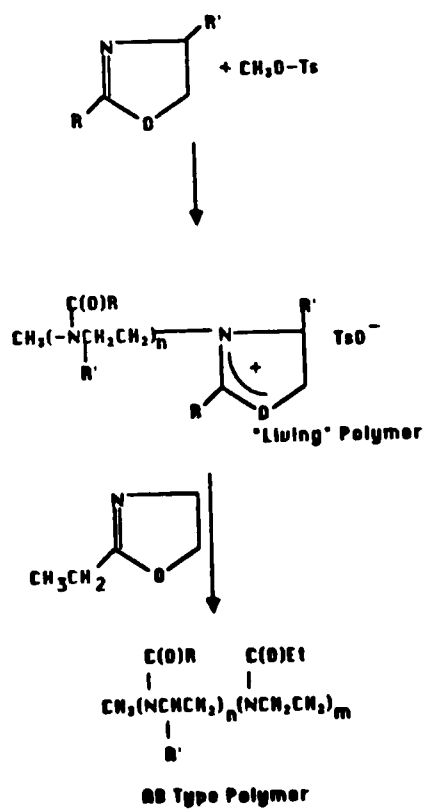
The oxazolines are polymerized by cationic ring-opening polymerization. These polymerizations are known to be "living" polymerizations thus allowing straight forward in situ synthesis of block copolymers. A wide range of oxazolines substituted at both the 2 and 4 positions have been polymerized by cationic ring-opening polymerization. Both electron withdrawing and electron donating substituents have been successfully used including some very bulky substituents. Commonly $Ts\text{-}OCH_2CH_2O\text{-}Ts\text{-}OCH_2CH_2O\text{-}Ts$ or bisoxazolium triflate are used as initiators.

ABA polymers can be prepared that are composed of two different oxazolines or an oxazoline and some other polymer block. Polymers that are composed of two different oxazolines or are prepared by first polymerization of one of the oxazolines using an initiator such as $Ts\text{-}OCH_2CH_2O\text{-}Ts$ or bisoxazolium triflate from which both ends will grow simultaneously. Then the second oxazoline is added, polymerizing at the ends of the polymer chain. Since both ends of the chain are still "living", the polymer will grow from both ends. An AB or $(AB)_n$ polymers would be prepared in a similar fashion, using a mono-substituted initiator such as $CH_3O\text{-}Ts$.

Other blocks can be substituted into the polyoxazolines. The only requirement here is that the block be hydroxyterminated so that the hydroxy group can be used as a point of initiation for the polymerization of the oxazoline.

$$+ \ TsOCH_2CH_2OTs$$

(structure: oxazoline ring with R and R')

$$\downarrow$$

$$TsO^- \quad R' \quad \overset{\displaystyle C(O)R}{\underset{\displaystyle R'}{N-CH_2CH_2(NCHCH_2)_n}}-N \quad R' \quad TsO^-$$

"Living" Polymer

(4)

$$CH_3CH_2 \quad \text{(oxazoline ring)}$$

$$\downarrow$$

$$\overset{\displaystyle C(O)Et}{(NCH_2CH_2)_m}-\overset{\displaystyle C(O)R}{\underset{\displaystyle R'}{(NCHCH_2)_n}}-\overset{\displaystyle C(O)Et}{(NCH_2CH_2)_m}$$

—————————————————————

$$+ \ CH_3O{-}Ts$$

(structure: oxazoline ring with R and R')

$$\downarrow$$

$$CH_3(-\overset{\displaystyle C(O)R}{\underset{\displaystyle R'}{NCH_2CH_2})_n}-N \quad R' \quad TsO^-$$

"Living" Polymer

(5)

$$CH_3CH_2 \quad \text{(oxazoline ring)}$$

$$\downarrow$$

$$CH_3\overset{\displaystyle C(O)R}{\underset{\displaystyle R'}{(NCHCH_2)_n}}\overset{\displaystyle C(O)Et}{(NCH_2CH_2)_m}$$
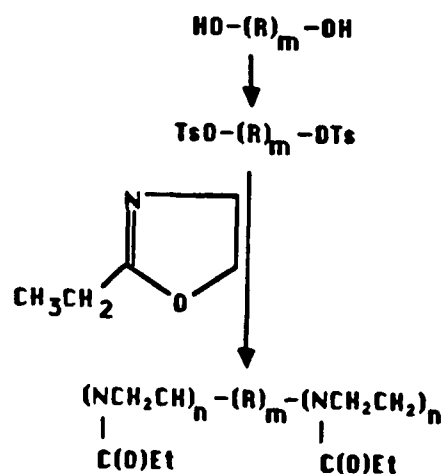
AB Type Polymer

Several polyoxazines ($[(CH_2)_3N(COR)]_n$, including ABA and AB block copolymers with oxazolines of other hydroxy-terminated polymers, have been prepared. The polymerization reactions are similar to those for the oxazolines, however, here radical initiators can also be used.

Several routes have been developed for the synthesis of the oxazoline monomers. They can be prepared from dehydrohalogenation of haloamides, dehydration of hydroxyamides, isomerization of N-acylaziridines and cyclization of amino alcohols with isocyanide.

However, despite the superior energetic properties of Compound 1, we have found that it does not have the necessary mechanical properties to make an excellent binder by itself. Compound 1 has no melting point, decomposing above 260°C. Because there is no melting point, it would be impossible to process of any formulation containing compound 1. Ideally, the polynitramine should be processable at 100°C for a binder application. Consequently, the future program of research will concentrate on preparation of thermoplastic elastomers with polynitramine blocks.

$$
\begin{array}{c}
HO-(R)_m-OH \\
\downarrow \\
TsO-(R)_m-OTs
\end{array}
$$

(6)

$$
(NCH_2CH)_n-(R)_m-(NCH_2CH_2)_n
$$
$$
\overset{|}{C(O)Et} \qquad \overset{|}{C(O)Et}
$$

R = Polyethylene glycol, Hydroxyterminated polyethylene Ohetones, THF, NAMN, BNRMO, BNMO, NMMO, etc

FUTURE RESEARCH

Our success with the model reaction, nitrolysis of poly[ethyloxazoline] to yield poly[N-nitroethyleneimine] to yield poly[N-nitroethyleneimine] or $[N(NO_2CH_2CH_2]_n$, enables us to envisage the synthesis of a large variety of polymers containing the nitramine functionality in an application as binders. We will tailor the properties of the binder by copolymerization methods. We will here draw on Dow's experience in oxazoline chemistry and our experience in synthesis of ABA block copolymers. There are several oxazoline copolymers that could be prepared to give modified properties of the final polynitramine.

The following classes of polymers containing the nitramine functionality are representative of the numerous possibilities.

(1)   Oxazoline-oxazoline ABA or $(AB)_n$ block copolymers.

(2)   Oxazoline-polyether-oxazoline ABA block copolymers. The ether blocks could be based on poly(epichlorohydrin) or polyoxetanes.

(3)   Oxazoline-polyethylene-oxazoline ABA block copolymers.

(4)   Oxazoline-Oxazine ABA or $(AB)_n$ block polymers.

Our strategy will allow tailoring of the properties of the final polymer through variation of the blocks in the ABA or $(AB)_n$ copolymers while maintaining the energy content by inclusion of the poly[nitramino] group. Additionally, we can include either energetic or non-energetic functionality in the side-chains as is appropriate. We envisage incorporation of energetic functional groups such as $CH_2C(NO_2)_3$, $CH_2CF(NO_2)_2$, or $CH_2CF_2NO_2$ as the side chains of some of our blocks. Such groups will act as an internal plasticizer in addition to increasing the energy content of the polymer.
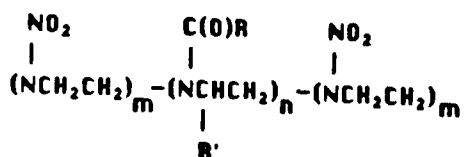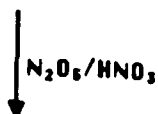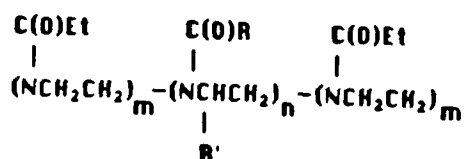
The proposed synthesis of these energetic copolymers is described below:

1. <u>Oxazoline-Oxazoline ABA and $(AB)_n$ Block Copolymers</u>. Because the cationic ring opening polymerization is a "living" polymerization, oxazoline block copolymers can be synthesized easily as was demonstrated using a bifunctional initiator in e pioneering work of Saegusa et al. and Litt et al (eq. 4 and 5).
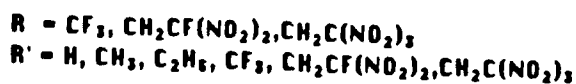
The groups R and R' will be selected such that only R' undergoes nitrodeacylation during

the reaction with N_2O_5/HNO_3. Such an outcome can be ensured by synthesizing oxazolines where the R group is electron withdrawing, CF_3, CH_2NO_2, $CH_2CF_2NO_2$, $CH_2CF(NO_2)_2$, $CH_2C(NO_2)_3$. The electron withdrawing group will destabilize the incipient acylium cation, thereby preventing deacylation. These electron withdrawing groups will not only prevent deacylation of the desired blocks, but will also contribute to the energetics of the binder material due to the presence of nitro groups in the side chain. Nitrolysis of these block copolymers will result in the synthesis of the desired binders containing the nitramino hard blocks.

Addition of substituted oxazolines, at the 2 or 5-position by methyl or other substituents, in the polymer backbone lowers the glass transition temperature of the polymer. The two monomers could be mixed together and polymerized to yield random copolymers. Similarly, replacement of oxazoline by oxazine or substituted oxazines will have a similar effect on the glass transition temperature and the melting point of the resulting polymers.
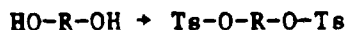
$$
\begin{array}{ccc}
\text{C(O)Et} & \text{C(O)R} & \text{C(O)Et} \\
| & | & | \\
(NCH_2CH_2)_m & -(NCHCH_2)_n- & (NCH_2CH_2)_m \\
& | & \\
& R' &
\end{array}
$$

$$\Big\downarrow N_2O_5/HNO_3$$

$$
\begin{array}{ccc}
\text{NO}_2 & \text{C(O)R} & \text{NO}_2 \\
| & | & | \\
(NCH_2CH_2)_m & -(NCHCH_2)_n- & (NCH_2CH_2)_m \\
& | & \\
& R' &
\end{array}
$$
(7)

$R = CF_3, CH_2CF(NO_2)_2, CH_2C(NO_2)_3$
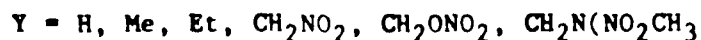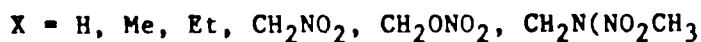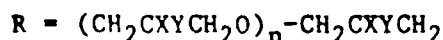$R' = H, CH_3, C_2H_5, CF_3, CH_2CF(NO_2)_2, CH_2C(NO_2)_3$

Similarly, the $(AB)_n$ polymers will be synthesized by sequential, alternative addition of the two monomers to the ethylene ditosylate initiator. The molecular weights of the blocks and the polymers can be controlled by altering the stoichiometry of the initiator and the monomers.
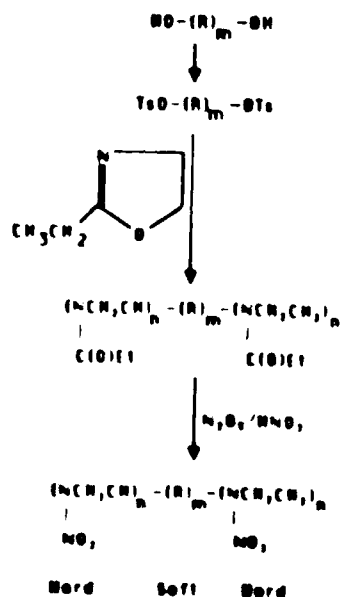
Oxazoline-Polyether-Oxazoline Block Copolymers. These block copolymers can be synthesized easily by using a bis-hydroxy terminated polyether block as the initiator. We can consider using the energetic or non-energetic ponyoxetanes or non-energetic polyethers.

$$HO-R-OH \rightarrow Ts-O-R-O-Ts$$

where:

$R = (CH_2CXYCH_2O)_n-CH_2CXYCH_2$

$X = H, Me, Et, CH_2NO_2, CH_2ONO_2, CH_2N(NO_2CH_3$

$Y = H, Me, Et, CH_2NO_2, CH_2ONO_2, CH_2N(NO_2CH_3$

Using these macro initiators, the block copolymers will be synthesized as indicated for a polyoxetane initiator:

(R

B - Polyethylene glycol Hydroxylterminated polyethylene
Oxetanes. THF, MRMN, BMBMB, BMMB, MMMMB, etc